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by Joshua Martin, Samuel G. Hirsch, Anit Giri, Mark H. Griep, and Shashi P. Karna

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT
Titanium dioxide nanotube (TiNT) arrays have been of intense interest to the alternative energies field in recent years, specifically dye-sensitized solar cell (DSSC) designs, due to their barrier-free, 1-D electron conduction pathway compared to the high number of grain boundaries and 3-D pathway of titanium dioxide (TiO_2) nanoparticles. In this work, highly ordered, densely packed, hexagonal TiO_2 nanotubes were synthesized in a single-step anodization of Ti foil using a constant dc potential of 60 V. The synthesized titania nanotubes exhibit a bamboo-like structure, with rings that form on uniform, discrete planes at a number of separation distances. Previous studies have noted that the separation distances as well as ring thickness can be controlled via alternating DC potential. However, it is clear that bamboo-ring nucleation sites in fact develop under constant voltage conditions and may serve as nucleation sites for larger, more distinct ring-like structures.

15. SUBJECT TERMS
titanium nanotubes, wide bandgap semiconductor, titanium dioxide, anatase, nanotubes, bamboo-like rings

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1. Introduction and Background

Ordered titanium dioxide (TiO_2) nanostructures, especially nanotubes and nanoparticles, have received a great deal of attention in recent years due to their application as efficient carrier transporters in dye-sensitized solar cells (DSSCs) (*1–3*). Considerable efforts have been made to synthesize highly aligned TiO_2 nanotubes (TiNT), which have a more efficient mode of electron transfer than nanoparticles due to reduced boundaries and a more uniform structure. A variety of methods have been used to prepare TiNT arrays utilizing ion track lithography (*4*), chemical precursor reactions (*5*), atomic layer deposition (*6*), rapid breakdown anodization and laser-drilled microhole array formation (*7*). However, among the various techniques used to form aligned TiNT arrays, the electrochemical anodization of Ti foil (*8-12*) is the most straightforward method of preparing highly ordered TiNT arrays with controllable dimensions. The anodic oxidation of Ti is appealing due to the reproducible control of the length, tube diameter, pore size, and thickness through applied voltage, time, and electrolyte composition (*13-16*). Previous studies demonstrate that the application of an alternating high and low voltage has led to bamboo-shaped TiNTs, showing fast tube growth during high voltage, slow growth during low-voltage application, and the formation of a compact initial oxide layer during the holding period (*3, 11*). It has been shown that TiNT with bamboo-like rings have increased surface area versus smooth walled tube, lending themselves towards increased DSSC performance, as well as improved utilization in other applications, such as H_2O splitting, photocatalytic degradation of pollutants, reduction of CO_2, etc. (*5*, *17*, *18*). It is important to note that hexagonal, closely packed, highly aligned TiNT structures are often made using a two-step process: a preliminary first-anodization to create a highly ordered hexagonal template and a second anodization that further etches the “dimples” left on the Ti surface after removing the initial oxide layers (*19–21*). In this report, we report the formation of highly ordered hexagonal, TiNTs with bamboo-type structure via a single-step, constant voltage anodization of Ti foil.

2. Experimental Procedure

Titanium dioxide nanotube arrays were grown using a single-step anodization process with a Ti foil working electrode (cathode) and a Platinum (Pt) foil counter electrode. The titanium foils (Sigma-Aldrich, 99.7%, 0.25 mm) were electrochemically anodized in a standard two-electrode cell using an Agilent E3649A DC power supply. The electrodes were kept at a fixed distance of 1.5 cm. The foils were first mechanically polished using a 9 μm diamond compound paste with a silk cloth and microid extender followed by a colloidal silica/wetted imperial cloth. The foil was then cut into 1 × 2 cm samples. The substrates were separately sonicated in acetone, isopropanol, and ethanol, each for 5 min using an ultrasonic cleaner (Branson 3510) before being rinsed with

deionized (DI) water. The anodization process was performed at 30, 40, and 60 V for 1–6 h using an electrolyte consisting of 0.25–0.5 wt.% ammonium fluoride (NH_4F) and 0.75–1.00 wt.% H_2O in ethylene glycol. The anodized samples were rinsed with DI water and then soaked in methanol for 30 s to initiate the detachment procedure. Free-standing TiNT membranes were separated from the Ti substrate by drying the methanol-wetted samples with a stream of nitrogen gas. This caused the freshly formed TiNT array to rapidly dry and delaminate from the substrate. To effectively remove the TiNT membranes for characterization, methanol wetting and nitrogen gas blowing were repeated several times.

To crystallize the amorphous TiNT arrays into the anatase phase, the arrays were annealed in a tube furnace at 723 K for 3 h using a heating rate of 20 Ks^{-1}. The structure and the morphology of the synthesized tubes were analyzed by powder x-ray diffraction (Rigaku TTRAXIII) and scanning electron microscopy (FEI NOVA NanoSEM).

3. Anodic Growth of TiO_2 Nanotube Layers

Nanotube formation in fluoride-ion-bearing electrolytes results from three simultaneously occurring processes (*22*, *23*): electric field-assisted oxidation of Ti metal to form TiO_2 (equation 1) (*2*, *3*), the chemical dissolution of Ti (equations 2 and 3), and the field-assisted dissolution of TiO_2 due to fluoride-ion etching as shown in the following chemical reactions:

$$Ti + 2H_2O - 4e^- \rightarrow TiO_2 + 4H^+, \quad (1)$$

$$Ti^{4+} + 6F^- \rightarrow TiF_6^{2-}, \quad (2)$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O. \quad (3)$$

When a voltage is applied, the amount of current gradually decreases as the oxide layer forms, according to equation 1, due to an increase in resistance. Once the TiO_2 layer has formed, the chemical dissolution of the oxide begins to compete with the anodic oxidation. The current finally becomes constant when the oxidation reaction and dissolution rates balance out and reach a steady-state. As the oxygen ions (O^{2-}) are transported from the solution to the Ti, titanium ions (Ti^{4+}) are transported from the titanium to the electrolyte interface and are dissolved into the solution via equations 2 and 3. These two dissolution mechanisms gradually etch selective pits in the oxide layer, which lead to the formation of nanotubes (*18*). As the anodization time increases, all three processes continuously increase the depth of the pores (pits) and produce highly ordered, vertically aligned nanotubes (*24*, *25*).

4. Results and Discussion

The x-ray diffraction (XRD) patterns for the as-prepared and the annealed samples are shown in figure 1. As seen from the XRD pattern, the as-prepared sample is amorphous whereas the annealed sample is crystalline anatase. It has been reported that the crystallinity of the nanotubes has a direct effect on the electrical and optical performance of the nanotube array (*22*, *26*).

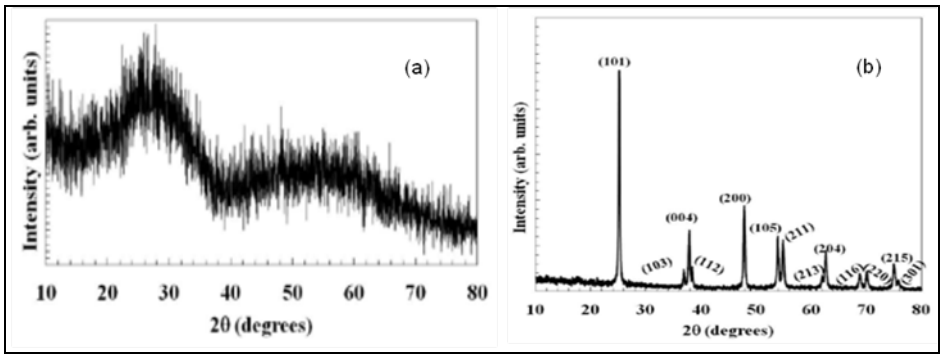

Figure 1. X-ray diffraction of (a) as-prepared TiO_2 nanotubes and (b) TiO_2 nanotubes annealed at 723 K for 3 h.

Furthermore, figure 2 shows a differential scanning calorimetry thermogram measurement displaying an exothermic crystallization peak (anatase) at 560 K of the as-prepared sample, which further confirms the amorphous nature of the as-prepared sample.

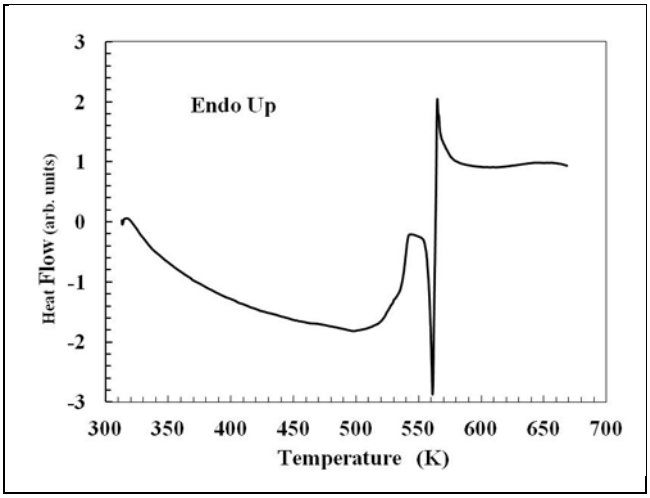

Figure 2. Differential Scanning Calorimetry (DSC) thermogram of as-prepared TiO_2 nanotube sample.

Scanning electron microscopy images in figure 3 display a profile view of the highly organized structure, a view of the bottom of the closely packed nanotube array, the open pores of the nanotube structure, and the “dimples” left on the top of the Ti metal substrate after removal.

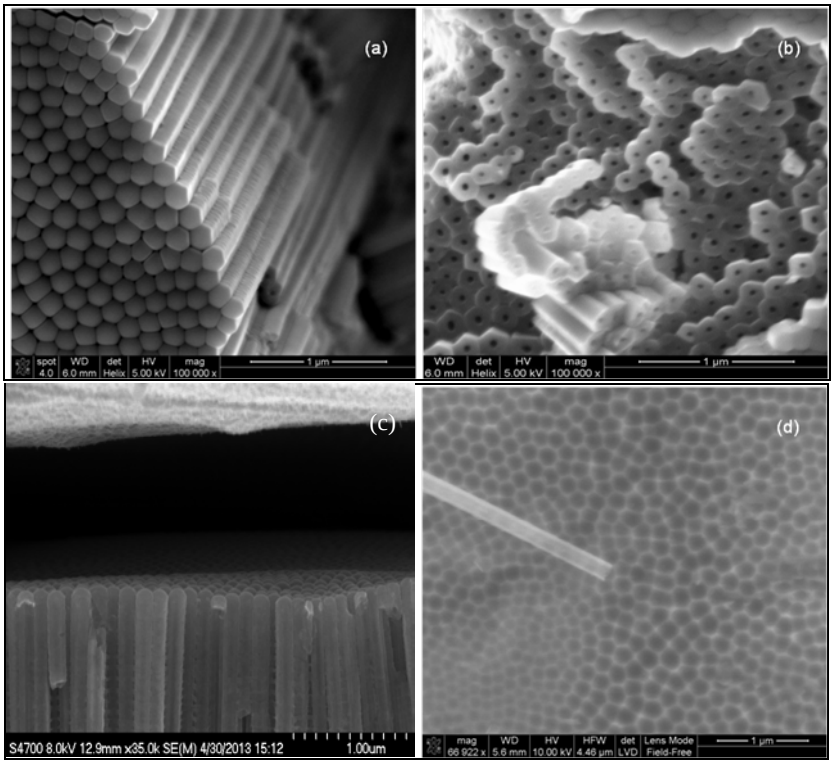

Figure 3. Scanning electron micrographs of (a) side profile view of hexagonal, highly oriented nanotube array, (b) bottom view of the array closely packed array, (c) bottom of nanotube array separated from the Ti substrate, and (d) top of Ti metal substrate after removing the nanotubes anodized at 60 V.

These images reveal the closely packed nature of the array. A closer look reveals highly aligned, densely packed, hexagonally oriented nanotube arrays that exhibit bamboo-like rings, which is closely shown in figure 4. Although the bamboo-like rings do not form at constant distances along the length of the tubes, they appear to be growing uniformly and on distinct planes. These rings appear to aid in the highly aligned and closely packed nature of the array by acting as a connection matrix for the nanotubes. The nanotubes shown in figures 3 and 4 were anodized for 4 h and have an approximate length of 18 μm with a tube wall thickness of 64 nm and a pore diameter of 32 nm at the Ti metal interface. The array growth rate was roughly 1.3 nm/s whereas the bamboo rings had a growth rate of approximately one ring every 40 s (0.025 Hz) with a separation distance of approximately 50 nm.

In order to further verify that bamboo-like rings indeed form at constant voltages, another anodization experiment was conducted using an electrolyte of 0.5 wt.% NH_4F and 1% H_2O in

ethylene glycol. A constant voltage was verified by using a Keithly 6430 to measure voltage vs. time, displayed in figure 5. Figure 6 shows the Scanning Electron Microscope (SEM) images confirming the growth of bamboo-like structures using a one-step, constant voltage anodization. The bamboo rings displayed in figure 4 have a separation distance of approximately 33 nm.

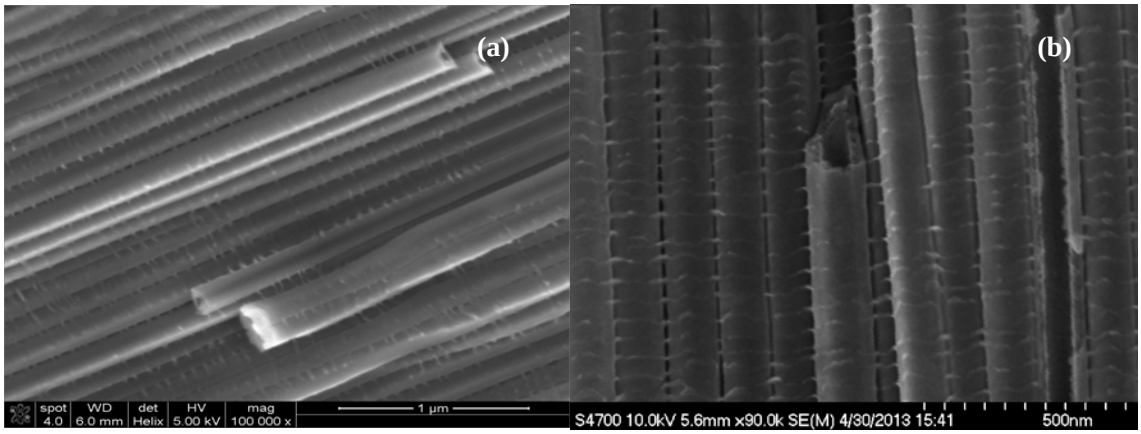

Figure 4. SEM images of the side view of TiO_2 nanotubes anodized at (a) 60 V and (b) 40 V.

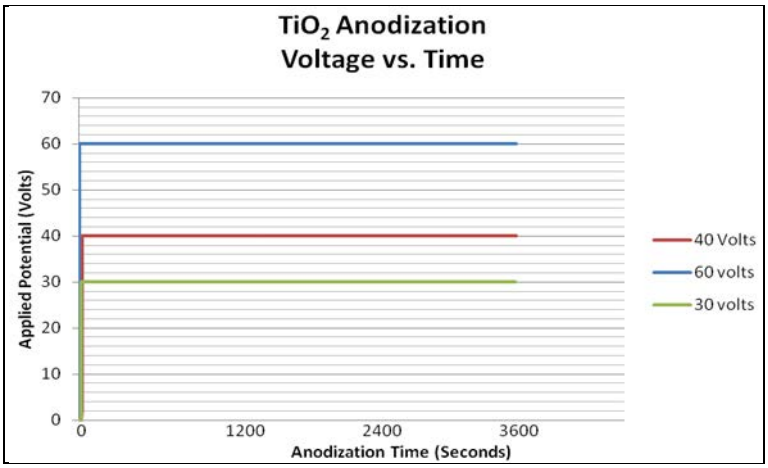

Figure 5. Voltage vs. time monitoring during the anodization of TiO_2 nanotubes.

The growth mechanism and composition of bamboo-like rings on TiO_2 nanotubes are not fully understood and have been attributed to alternating voltage. It has been proposed (*11*, *17*) that the bamboo-like rings are composed of a compact oxide. This is most likely caused by the oxidation reaction temporarily dominating the dissolution reactions, resulting in residual oxide. We propose that the bamboo-like structure is a result of the competing nature of the dissolution and oxidation reactions. When the oxidation reaction dominates over the dissolution rate, rings form along a distinct plane. This corresponds with previous studies, which apply an alternating potential to control the frequency that the rings occur. Because the reactions are heavily driven

by the applied voltage, alternating the potential changes the rate at which the reactions occur. Therefore, the size and spacing of the bamboo-like rings will change with different voltage levels and time delays.

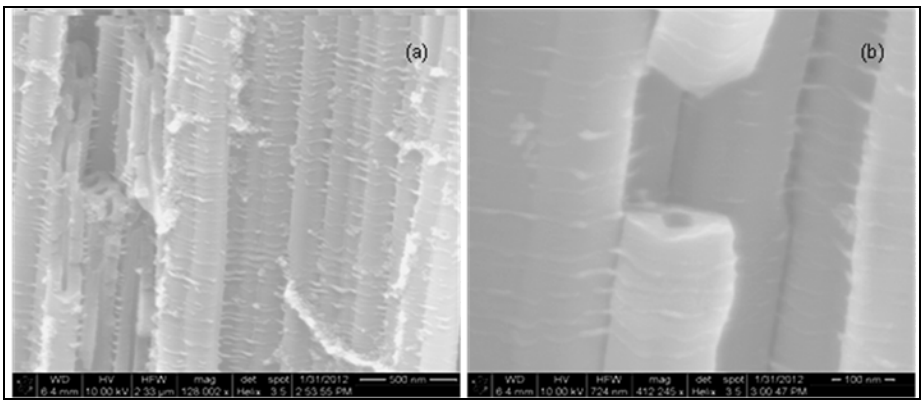

Figure 6. (a) Scanning electron microscopy images of TiO_2 nanotubes with bamboo-like rings, anodized at 40 V, 0.5% NH_4F and 1% H_2O under constant voltage and (b) close-up image of bamboo-like ring formations.

5. Conclusions

Highly ordered, densely packed, hexagonally oriented TiNTs were synthesized by a one-step anodic oxidation of Ti foils by applying a constant DC voltage. The tubes exhibit bamboo-like structure with rings formed at nearly equal distances along the length. Bamboo-like ring growth during constant voltage shows that the formation of nanotubes with bamboo-like rings is not caused by alternating the anodization potential. Controlling the growth of these nucleation sites can lead to nanostructures with definite advantages. Further studies on the composition of the oxide rings may elucidate how these structures can be further controlled and applied to other nanomaterials.

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List of Symbols, Abbreviations, and Acronyms

DI	deionized
DSC	Differential Scanning Calorimetry
DSSC	dye-sensitized solar cell
NH_4F	ammonium fluoride
Pt	Platinum
SEM	Scanning Electron Microscope
TiNt	TiO_2 nanotubes
TiO_2	titanium dioxide
XRD	x-ray diffraction

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